Long-Range Transport of Hydrothermal Dissolved Zn in the Tropical South Pacific

Saeed Roshan^{1,*}, Jingfeng Wu¹, William J. Jenkins²

¹Rosenstiel School of Marine and Atmospheric Science, University of Miami,
Coral Gables, FL, USA 33124

²Woods Hole Oceanographic Institution, Woods Hole, MA 02543

*corresponding author: sroshan@rsmas.miami.edu

J. W. : jwu@rsmas.miami.edu

W. J. J.: wjenkins@whoi.edu

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Abstract

Zinc (Zn) is one of the essential micronutrients that can regulate oceanic primary productivity due to its central roles as a co-factor in carbonic anhydrase and alkaline phosphatase. However, the sources of dissolved Zn to the ocean are poorly understood, mainly because of the difficulties of sample collection and analysis for Zn at very low concentrations in oceanic waters. The prevailing view considers rivers as the major source of dissolved Zn to the ocean. Here we report the dissolved Zn section along a ~4500-km transect at approximately 15°S in the tropical South Pacific Ocean along the western segment of the US GEOTRACES EPZT cruise (the GP16 transect). Dissolved Zn exhibits a substantial enrichment emanating from the hydrothermal vents at the axis of the East Pacific Rise to the central South Pacific, ~4000 km away. Total dissolved Zn and mantle-derived ^3He show a correlation with $R^2=0.71$ at depths 2300-2800 m along the transect. It is likely that this correlation can be improved by accounting for the non-uniformity in the non-hydrothermal background of dissolved Zn. After subtracting the non-hydrothermal Zn imprint using Zn-Si relationship in the North Pacific, the correlation between “excess” dissolved Zn and mantle-derived ^3He improves significantly ($R^2=0.87$). The correlation leads to a global hydrothermal Zn flux of $1.75 \pm 0.35 \text{ Gmol yr}^{-1}$ that is many-fold higher than the input fluxes estimated by other studies. These results suggest that mantle-derived dissolved Zn dominates the oceanic Zn inventory and that dissolved Zn residence time is much shorter ($3,000 \pm 600$ years) than previous input-based estimates (11,000 and 5,0000 years) and more consistent with previous removal-based estimate (3,000-6,000 years). The shorter residence time, the dominance of hydrothermal input and the negligible contribution of dust to the oceanic

dissolved Zn inventory imply that changes in the efficiency of particle-associated removal according to changes in oceanic productivity through time may change the oceanic dissolved Zn inventory rapidly. This, in turn, may lead to a divergence between Zn and the nutrients whose oceanic inventories are more affected by dust which can change dramatically on glacial/interglacial timescales.

1. Introduction

Zn is one of the major micronutrients that plays a major role in regulating the biological uptake and transfer of inorganic carbon through its role in carbonic anhydrase (Anderson and Morel, 1978; Brand et al., 1983; Morel et al., 1994). Nonetheless, documentation of its role through field-based studies in iron-limited areas has been overshadowed by the overwhelming effects of iron addition (Coale et al., 2003). More recently, another major role of Zn has been observed in the metalloprotein alkaline phosphatase that functions in the utilization of dissolved organic phosphorous (DOP) (Shaked et al., 2006). As an example, the surface of the central North Atlantic is a region devoid of dissolved inorganic phosphate (DIP) (Wu et al. 2001), whilst the DOP concentrations are remarkably high (Mather et al., 2008). Therefore, the activity of Zn-modulated alkaline phosphatase can potentially regulate the uptake of this large pool of DOP and play a central role in the primary production of such areas. Mahaffey et al. (2014) have recently studied such control by Zn in a field study in the North Atlantic.

It is a long-standing view that rivers are the major source of dissolved Zn to the ocean (Shiller and Boyle, 1985; Little et al., 2014). The studies on fluvial dissolved Zn have always faced three issues: (1) the difficulties in sampling and analysis of riverine waters for very low levels of dissolved Zn concentration; (2) the fact that most of world's rivers are contaminated with anthropogenic Zn, precluding the valid estimation of the natural Zn flux which has supplied the ocean on geological timescales; and (3) that the processes that take place during the intrusion of fluvial Zn to the ocean at the estuaries may not be completely conservative. By studying relatively pristine (relatively unaffected by human activities) rivers, Shiller and Boyle (1985) estimated 0.2 Gmol yr^{-1} as the fluvial input of dissolved Zn to the ocean. Little et al. (2014) recently attempted to compute the input and removal fluxes of dissolved Zn to and from the ocean, assuming river and dust as the main sources of dissolved Zn to the ocean, and removal by adsorption on ferromanganese crusts and incorporation into sinking biogenic particulate carbonate as the major sinks of the oceanic dissolved Zn. They found an imbalance between sources and sinks, suggesting a missing removal process for the dissolved Zn. In a later study, Little et al. (2016) have identified and quantified a sink for dissolved zinc within the continental margins which can alleviate the projected imbalance in the previous study (Little et al., 2014).

One potential uncertainty in Little et al. (2014) is the estimate of the riverine dissolved Zn flux. Since dissolved Zn concentration varies substantially among the major world rivers (Gaillardet et al., 2003), choosing any subset of rivers can result in a different fluvial dissolved Zn flux. For example, by choosing the lower end of fluvial flux, Little et al. (2014) could balance the sources and sinks, or even estimate a removal in excess to input. Moreover, as mentioned above, the impact of anthropogenic effects on the riverine dissolved Zn content is an inevitable uncertainty in any fluvial flux estimation (Chen et al., 2008).

From a removal point of view, Little et al. (2014) have estimated the output flux as 0.35 Gmol yr⁻¹ by including ferromanganese- and carbonate-associated removals. Aside from carbonate-associated removal, Zn as a nutrient may undergo an oceanic removal similar to other macronutrients such as P, N, and Si through burial and preservation of organic and siliceous tissues in the seafloor sediment. Bruland et al. (1994) have estimated this removal at 1.2-2.4 Gmol yr⁻¹ (based on 3,000-6,000 years as their estimate of residence time) by simultaneous determination of acid-leachable particulate and dissolved Zn in the deep North Pacific. This removal estimate is much higher than both the input and output fluxes estimated by Little et al. (2014), suggesting a missing “source” in the oceanic inventory of dissolved Zn. In a recent study, Little et al. (2016) have estimated 0.56 Gmol yr⁻¹ as the preservation rate of Zn in marine sediments near the continents. This sink may include the removal through bioassimilation in the surface ocean, a removal mechanism which was overlooked in the budget balance by Little et al. (2014). Adding together all the removal fluxes considered by Little et al. (2014) and (2016) results in 0.91 Gmol yr⁻¹ which is, yet, relatively lower than the output flux estimated by Bruland et al. (1994) in the open ocean (1.2-2.4 Gmol yr⁻¹).

Overall, from all the studies, we can extract a range of the dissolved Zn oceanic residence time of 3-50 kyr and an according range of input/removal flux range of 0.2-2.4 Gmol yr⁻¹, indicating a large uncertainty in the estimates, which primarily results from these studies ignoring some inputs or outputs (Shiller and Boyle, 1985; Bruland et al., 1995; Little et al., 2014). One of the dissolved Zn inputs to the ocean which has never been well-constrained is hydrothermal flux.

Decades ago remarkable enrichment of dissolved Zn was observed in hydrothermal fluid, which led to the flux of 5.7-15 Gmol yr⁻¹ as estimated by Von Damm et al. (1985) through

studies on vent fluids. Elderfield and Schultz (1996) refined this estimate to 1.2-3.2 Gmol yr⁻¹. Even though this flux is remarkable compared to more recent input/output fluxes outlined above, hydrothermal dissolved Zn was not considered as a major player in the oceanic Zn cycle, likely due to the massively-overestimated fluvial flux of dissolved Zn at that time (>17 Gmol yr⁻¹; Broecker and Peng, 1982). Although further study on rivers refined the fluvial flux of dissolved Zn to a much lower value (Shiller and Boyle, 1985), years later, German et al. (1991) proposed that scavenging removal processes take place for some trace metals such as Zn near hydrothermal vents, which led to the reduction of hydrothermal flux of dissolved Zn to much lower values.

The lack of studies covering a large field around the hydrothermal vents and the reasons outlined above have led this input to be a neglected source of dissolved Zn to the ocean (Shiller and Boyle, 1985; Little et al., 2014). Dissolved Zn enrichment near the hydrothermal vents of the Mid-Atlantic Ridge (TAG) has recently been observed through a basin-scale survey (Conway and John, 2014a; Roshan and Wu, 2015), although a long-range transport of dissolved Zn was not evident in that basin. Basically, the hydrothermal activity of the TAG vent is insignificant, even when considering the ³He distribution which is a conservative tracer of hydrothermal activity (Jenkins et al., 2015; Bianchi et al., 2010). According to the ³He flux and the spreading rates, the Mid-Atlantic Ridge has the lowest hydrothermal activity compared to other ridges in other major basins (Bianchi et al., 2010). Hence, in order to estimate a more valid hydrothermal flux of elements (particularly within a global context), the vents on the axis of the East Pacific Rise (EPR) as the fastest spreading ridge on the world oceanic crust with a documented basin-scale transport of conservative hydrothermal tracer ³He (Lupton and Craig, 1981) can be more suitable study locations. In this study, we determined the dissolved Zn and ³He distributions

around the southern EPR to quantify the impact of hydrothermal vents as a source of dissolved Zn to the ocean using a high number of data points along a basin-scale section.

2. Sampling and Analysis

Trace metal seawater samples were collected with Teflon-coated GO-FLO bottles mounted on a plastic-coated rosette carousel (Cutter and Bruland, 2012) aboard the RV *Thompson* during the US GEOTRACES cruise in October-December 2013 (transect GP16 from Manta-Ecuador to Papeete, French Polynesia). In this study, we analyzed the samples collected in the western segment of the GP16 transect which covers the leg from the axis of the EPR ($\sim 112^\circ\text{W}$) to the central South Pacific ($\sim 150^\circ\text{W}$) as shown in Figure 1. The collected samples were passed through acid-washed 0.2- μm pore Acropak Supor capsule filters (Pall). For each sample, a certain amount of filtrate was discarded at the beginning of the filtration in order to condition the capsule filters before collecting the filtered samples. The filtered samples were stored in pre-cleaned 0.5-L LDPE bottles (cleaning progression: 1% soap, 10% clean HCl and then 0.5% ultraclean HNO_3) and were transported to the land-based laboratory at the University of Miami where the samples were acidified using ultraclean concentrated nitric acid to $\text{pH}\sim 1.8$ and stored at room temperature for over two months prior to analysis.

Zn concentration in the samples was determined using the $\text{Mg}(\text{OH})_2$ co-precipitation isotope dilution inductively coupled plasma mass spectrometry (ICP-MS) method, a modified version of Wu and Boyle (1997) using the spike solution enriched with ^{68}Zn and a multi-collector ICP-MS (Thermo Neptune) at the University of Miami. The same method has been applied by Roshan

and Wu (2015) to determine the dissolved Zn distribution in the North Atlantic Ocean along the GEOTRACES GA 03 transect. The method has a detection limit of ~ 0.03 nM and a precision of $\sim 3\%$ at 1.0 nM dissolved Zn. Silicate concentration was determined on the ship routinely during the cruise by the Ocean Data Facility (ODF) group using a Seal Analytical continuous flow Autoanalyzer as described elsewhere (Armstrong et al., 1967).

Figure 1. The locations of sampling stations occupied during this study. These stations are a subset of stations undertaken by the US GEOTRACES EPZT cruise that forms the western leg of the cruise with emphasis on the basin-scale impact of the East Pacific Rise hydrothermal field.

The helium samples (~ 45 g each) were obtained on separate but co-located casts. They were drawn from the standard rosette (12-position, 30 liter Niskin bottles) using TYGON tubing connected to lengths of $5/8''$ soft copper refrigeration tubing and hydraulically crimp-sealed (Young and Lupton, 1983). On shore, gasses from the samples were quantitatively vacuum-

extracted into liquid nitrogen chilled ~25 cc aluminosilicate glass flasks and sealed prior to analysis. Sample processing on the mass spectrometer system included purification over SAES® getters to remove reactive gases and using cryogenics to separate the noble gases (Lott and Jenkins, 1984; Lott, 2001; Stanley et al., 2009). Sample integrity was evaluated using noble gas abundances (not reported here), and was determined by quadrupole mass spectrometer with an accuracy of 0.2 to 0.3% depending on the gas. The helium abundance and isotope ratio ($^3\text{He}/^4\text{He}$) were determined using a branch-tube magnetic sector mass spectrometer to an accuracy of 0.15% or better, as determined by reproducibility of standards and duplicate samples. The isotope ratio was referenced to an atmospheric standard.

Mantle-derived ^3He ($^3\text{He}_{\text{mantle}}$) is computed as an approximate measure of the non-atmospheric ^3He over saturation:

$$^3\text{He}_{\text{mantle}} = (\delta^3\text{He} - \delta^{*3}\text{He})/100\% \times C[\text{He}] \times 1.384 \times 10^{-6} \quad (1)$$

Where the measured helium isotope ratio anomaly $\delta^3\text{He} = (R_x/R_A - 1) \times 100\%$, R_x and R_A

are the $^3\text{He}/^4\text{He}$ ratios of the sample and air (1.384×10^{-6}) and $\delta^{*3}\text{He}$ is the helium isotope ratio anomaly in solubility equilibrium with the atmosphere. The latter is a weak function of temperature (Benson and Krause, 1980) and is typically around -1.8% for the data used here.

$C[\text{He}]$ represents the concentration of helium. The ^3He data included in this study has previously been plotted and shown by Resing et al. (2015). The data of this study can be found in the online supplementary material (Appendix).

3. Results and Discussion

Dissolved Zn concentration along the transect is low (<0.1 nM) in the surface mixed layer (Fig. 2a), increases with depth to a maximum of ~ 8.5 - 9.0 nM at 2300-2800 m and then decreases to ~ 8.0 nM below 3000 m (Fig. 2b). The tongue of dissolved Zn maximum extends westward from the hydrothermal vents near the EPR located at the eastern edge of the transect (Fig. 1) to the central South Pacific gyre. The Zn maximum coincides with the maximum of mantle-derived ^3He , a conservative hydrothermal tracer (Fig. 2c), indicating a possible dissolved Zn source emanating from the hydrothermal vents near the mid-ocean ridges at the axis of EPR. However, some fraction of this dissolved Zn can be carried to the transect via the Pacific Deep Water (PDW; Reid (1997)) from the North Pacific where dissolved Zn exhibits its highest oceanic concentrations (Bruland, 1980; Conway and John, 2015). This is also evident in the silicate distribution observed for the same samples that shows enrichment at 2000-4000 m (Fig. 2d). The distribution of the Apparent Oxygen Utilization (AOU), as the indicator of oxygen consumption driven by microbial degradation of organic tissues, shows that the low-oxygen aged water (i.e. high AOU) from the North Pacific has a great influence within 2300-2800 m (Fig. 2e).

Figure 2. Distribution of dissolved Zn in upper 1000 m (a), dissolved Zn in the entire water column (b), mantle-derived ^3He (c), silicate (d), AOU (e) and excess Zn (f) along the western segment of the GP16 transect.

The dissolved Zn vs. mantle-derived ^3He plot shows a positive correlation with slope $2.64 (\pm 0.0.19) \times 10^6$ (Fig. 3a) and $R^2=0.71$. It is readily evident in the dissolved Zn distribution within 2300-2800 m that the dissolved Zn plume displays a longer tongue than mantle-derived ^3He (Fig. 2b&c). This suggests that a portion of the dissolved Zn enrichment within 2300-2800 m may be emanating from the North Pacific through meridional flow (Reid, 1997) rather than hydrothermal activity at the southern EPR. Hence, accounting for this non-hydrothermal dissolved Zn may lead to a stronger correlation between the dissolved Zn and ^3He . The component of this North Pacific-originated pool of dissolved Zn could not affect the correlation if it acquired a relatively “uniform” value within 2300-2800 m along the transect. However, as it is shown in the silicate distribution (Fig. 2d), the regenerated component of silicate may not be uniform along the entire transect at 2300-2800 m, suggesting a similar pattern for that of dissolved Zn. The non-uniformity of the non-hydrothermal background, in contrast, does not seem to affect the dissolved Fe- ^3He and Mn- ^3He correlations, allowing Resing et al. (2015) to observe strong correlations for these elements in the majority of our transect (GP16) without correcting for background imprints. However, dissolved Zn and macronutrients (more specifically Si) distribution patterns show a higher degree of similarity than those observed

between dissolved Fe or Mn and macronutrients (Bruland, 1980), necessitating the background correction to study the sole imprint of hydrothermal activity on the dissolved Zn distribution.

The observed correlation between dissolved Zn and silicate in the North Pacific (Bruland, 1980, Conway and John, 2015) can be used to correct the regeneration background at 2300-2800 m along our transect in the South Pacific. This is because a major fraction of the regenerated component of dissolved Zn, silicate and other micronutrients along the mentioned depth range probably emanates from the North Pacific through PDW (Reid, 1997). Khatiwala et al. (2012) have also derived the presence of old waters at the mentioned depth range in the tropical South Pacific which emanates from the North Pacific. Since different water masses might have a different Zn-Si relationship (Roshan and Wu, 2015), it is essential to apply the Zn/Si ratio from the North Pacific to subtract the regeneration background from the total dissolved Zn signal via the following relationship:

$$Zn_{excess} = Zn_{GP16} - Zn:Si_{N.Pacific} \times Si_{GP16} \quad (2)$$

Where excess Zn (Zn_{excess}) is hypothesized to be the fraction of dissolved Zn “variability” that is controlled by non-regeneration processes, such as hydrothermal activity. Inasmuch as we are examining the correlations against mantle-derived ^3He , we need the variability to be governed by hydrothermal activity, otherwise the “absolute” value of excess Zn may not reflect the exact hydrothermal-driven dissolved Zn concentration. Zn_{GP16} and Si_{GP16} are the dissolved Zn and silicate concentrations as determined in this study. $Zn:Si_{N.Pacific}$ represents the Zn:Si ratio determined in the seawater samples collected from the North Pacific. There are few studies determining dissolved Zn in the open-ocean of the North Pacific. The most offshore profiles of

dissolved Zn and silicate have been reported at stations very close together at ~30 °N, 140 °W by Bruland (1980) and later by Conway and John (2015). The Zn/Si ratio determined for the 1500-3055 m, the depth range where PDW has the greatest influence, from the data of the former study is 0.052 ± 0.002 (1σ) nmol/ μ mol (Bruland, 1980). Conway and John (2015) have found a similar ratio, 0.055 ± 0.001 nmol/ μ mol within this depth range (only 6% higher). By merging the data from these two studies into one data set, we derived 0.053 ± 0.002 nmol/ μ mol as the best estimate of the Zn/Si ratio of the open-ocean North Pacific at the depth range dominated by PDW. Janssen and Cullen (2015) have recently reported decoupling between dissolved Zn and silicate in the high-latitude North Pacific near the low-oxygen zone. Nonetheless, the Zn-Si correlation and ratio from the two former studies (Bruland, 1980; Conway and John, 2015) might be a better representative of the entire North Pacific. Note that in order to make this ratio applicable on our data set, we apply the typical deep seawater density 1.0275 kg/L (unit-adjusted ratio = 0.0545 nM/ μ mol/kg).

The distribution of excess Zn, as calculated via Equation (2) is shown in Figure 2f. The correction for the background non-uniformity truncates the hydrothermal Zn plume and makes it more similar to the hydrothermal tracer mantle-derived ^3He than that of the total dissolved Zn. The excess Zn vs. ^3He plot (Fig. 3b) also displays a much stronger correlation ($R^2=0.87$ vs. $R^2=0.71$), suggesting that, as predicted above, the non-uniformity of non-hydrothermal background can be an artifact in investigating the hydrothermal Zn plume. The slope of excess Zn vs. ^3He is higher than that of total dissolved Zn vs. ^3He (3.32×10^6 vs. 2.64×10^6) particularly due to moderating the Zn concentrations at the western edge of the plume, where a significant fraction of Zn can be governed by mixing of the regenerated pool from the North

Pacific (Fig. 2b&c). Note that we applied a Type II weighted regression for all regressions performed in this study (Glover et al., 2011). The deviation arising from the uncertainty of the North Pacific Zn/Si ratio (± 0.002) and the uncertainty associated with the total dissolved Zn determination were propagated into the excess Zn results before conducting the regression shown in Fig. 3b.

There are a few studies on the pattern of currents in the tropical South Pacific which use the available hydrographic data and geostrophic dynamics (Reid, 1997; Talley and Johnson, 1994; Hautala and Riser, 1993). Although these studies have been carried out on low-resolution hydrographic observations which were available more than two decades ago, a main westward current has been inferred. Nonetheless, it appears that the distribution of ^3He concentration or its ratio to ^4He are the most powerful properties to discern the flow pattern in the tropical South Pacific, given that ^3He has a known source location (i.e. EPR) and that it does not undergo any in-situ reactions. From $^3\text{He}/^4\text{He}$ observations made decades ago, it has been well-documented that westward currents dominate the horizontal component of streams at the depth range of the EPR (Lupton and Craig, 1981). The ^3He concentration distribution determined in this study repeats the same feature (Fig. 2c).

However, a discontinuity can be seen at 120°W within the EPR depth range (2300-2800 m) in the distributions of many hydrothermally-sourced elements or isotopes including the mantle-derived ^3He (Fig. 2c), total dissolved and excess Zn (Fig. 2a&f), and dissolved manganese and iron (Resing et al., 2015) along the GP16 transect. This suggests that our study region (particularly $\sim 120^\circ\text{W}$) may be affected by a meridional transport of water emanating from a region with lower hydrothermal influence. Distributions of silicate and Apparent Oxygen Utilization (AOU) along our transect exhibit a consistent feature (Fig. 2d&e).

The distal transport of hydrothermal Zn from the EPR is surprising because Zn has been classified as one of the hydrothermally-unimportant trace metals which may undergo an efficient removal during the precipitation of Zn sulfide (ZnS) within the hydrothermal plume (Elderfield and Schultz, 1996; German and Seyfried, 2014). The first study on the dissolved phase of metals within hydrothermal plumes demonstrated a remarkable enrichment of dissolved Zn near the vent (Von Damm et al., 1985). A later study, but on the “particulate” phase, showed that particles sampled near the vent are enriched in Zn (German et al., 1991). The presence of the Zn-rich particles convinced German et al. (1991) to consider Zn as a metal similar to Fe that undergoes a substantial scavenging removal near the hydrothermal vent. The correlation between particulate Zn and particulate Fe inside the hydrothermal plume shows a concavity toward lower particulate Zn (German et al., 1991). This type of correlation indicates one of two possibilities: sinking of Zn-rich particles to the seafloor is faster than that of Fe-Rich particles; or Zn is leaving the particulate phase to the dissolved phase whilst Fe is more stabilized in the particulate phase. Our observation, which indicates an efficient mobility of hydrothermally-induced dissolved Zn, is more consistent with the latter process. Note that there has been some tendency to introduce hydrothermal activity as a considerable source of dissolved Zn to the ocean in some later studies. For example, Wheat et al. (2002) have performed a budget compilation for dissolved Zn input to the ocean and estimated a hydrothermal flux (from nearfield data) of 13 fold higher than the fluvial flux.

The lack of convexity/concavity in the excess Zn vs. ^3He plot suggests minimal removal of dissolved Zn during the dispersion of hydrothermal plumes on basin-scale distances (Fig. 3b). It also indicates that if more than one vent end-member affects the Zn distribution along the

transect (which is possible over ~4,500 km), the other end-members have similar Zn:³He ratios. The uniform Zn:³He relationship allows for a “reliable” estimate of hydrothermal dissolved Zn input based on the Zn:³He ratio of $3.32 (\pm 0.15) \times 10^6$ obtained from the slope of the linear excess Zn-³He plot (Fig. 3b) and recent estimates of the global mantle ³He flux of 527 ± 102 mol yr⁻¹ (Bianchi et al., 2010). A flux of 1.75 ± 0.35 Gmol yr⁻¹ can be computed as the global hydrothermal flux of dissolved Zn to the ocean. In contrast to Zn, Fe and Mn have been shown to have different ratios to the ³He concentration for the stations near the vent compared to the stations located farther along the GP16, precluding a reliable estimation of global hydrothermal input (Resing et al., 2015).

As mentioned above, even though dissolved Zn shows a hydrothermal enrichment near TAG (Roshan and Wu, 2015), due to low flux from the Mid-Atlantic Ridge (Bianchi et al., 2014; Jenkins et al., 2015), it is not possible to calculate a reliable hydrothermal flux of Zn, nor other trace metal such as iron and manganese (Hatta et al., 2015). The Zn/³He ratio calculation without linearization on the few data points with high ³He (station USGT11-16 in Roshan and Wu (2015)), after background subtraction for both dissolved Zn and ³He, shows a variety of ratios from 4 to 7×10^6 . However, a linear correlation cannot be discerned.

Figure 3. Total dissolved Zn (a) and excess Zn (b) against mantle-derived ^3He . The data points at the depths 2300-2800 m for all stations ($n = 81$) have been included in this plot.

The hydrothermal Zn flux estimated in our study is much higher than the fluvial dissolved Zn flux estimated from the dissolved Zn concentration in riverine waters. Hydrothermal dissolved Zn flux to the ocean is approximately 8, 5 and 3 fold higher than the fluvial flux estimates by Shiller and Boyle (1985), Gaillardet et al. (2003) and Little et al. (2014), respectively. The atmospheric deposition flux of Zn to the ocean is more than ~ 10 fold lower than fluvial and hydrothermal fluxes. A simple calculation applying 450 Tg yr^{-1} as the global flux of dust to the ocean, 68 ppm as the crustal abundance of Zn and 15 % as the solubility of Zn from dust particles in seawater would result in a flux of $0.069 \text{ Gmol yr}^{-1}$ (see Little et al. (2014) and references therein). Therefore, hydrothermal activity is the dominant source of dissolved Zn to the ocean.

Although our new estimation of hydrothermal dissolved Zn flux suggests a dominant source, it is, yet, lower than the fluxes estimated through the studies on the vent fluid such as 5.7-15 Gmol yr⁻¹ by Von Damm et al. (1985). As first proposed by German et al. (1991), this suggests that the particle-associated processes near the vent may be at play in reducing the efficiency of hydrothermal dissolved Zn input to farther regions. However, Figure 3b shows that there is minimal removal of hydrothermally-added dissolved Zn from proximal to distal regions. In addition, in a later estimation from the nearfield studies (dissolved Zn concentration ~40-100 μM compared to ~10 nM as the highest concentration obtained in our study), Elderfield and Schultz (1996) reduced the hydrothermal dissolved Zn flux to 1.2-3.2 Gmol yr⁻¹. This range of estimated flux encompasses our estimate (1.75 ± 0.35 Gmol yr⁻¹), indicating that the removal of hydrothermally-added dissolved Zn may not be an efficient process as the vent fluid is diluted from concentrations of the order of tens of μM to few nM (range of dissolved Zn concentration in the open ocean).

Accounting for the hydrothermal source in the oceanic mass balance of dissolved Zn indicates that the residence time of dissolved Zn in the ocean must be much lower than the previous input-based estimates. The first estimate for dissolved Zn residence time in the ocean was 50,000 years (Shiller and Boyle, 1985). Little et al. (2014) have recently reduced this to 11,000 years by choosing another subset of rivers and taking dust input into account (total input flux = 0.66 Gmol yr⁻¹). Little et al. (2014) calculated a fluvial flux based on a subset of rivers (0.83 Gmol yr⁻¹) and considered that as the higher end of a range whose lower end is the flux calculated by Gaillardet et al. (2003) (0.35 Gmol yr⁻¹). They then took the average as the best estimate (0.59 Gmol yr⁻¹). In order to quantify the uncertainty associated with the fluvial estimation and to combine this uncertainty with that of hydrothermal flux (± 0.35 Gmol yr⁻¹),

we need a standard deviation instead of a range. Hence, we calculated $\pm 0.3 \text{ Gmol yr}^{-1}$ as the standard deviation of the total fluvial input by Little et al. (2014) from their tabulated riverine concentrations. Since the standard deviation for the fluvial flux computed by Gaillardet et al. (2003) is not known, we take $\pm 0.35 \text{ Gmol yr}^{-1}$ as the standard deviation for the best estimate proposed by Little et al. (2014) (i.e., best fluvial flux estimate = $0.59 \pm 0.35 \text{ Gmol yr}^{-1}$). Note that since the dust flux of Zn is negligible ($0.069 \text{ Gmol yr}^{-1}$), we do not consider any standard deviation for this term.

Adding hydrothermal flux from our study to the inputs considered by Little et al. (2014) and the propagation of uncertainties result in $2.41 (\pm 0.5) \text{ Gmol yr}^{-1}$ as the total input of dissolved Zn to the ocean which corresponds to a residence time of 3,000 (± 600) years. Little et al. (2014) have found that even the fluvial and dust inputs are $0.31 \text{ Gmol yr}^{-1}$ in excess to the ferromanganese- and carbonate- associated sinks. Adding hydrothermal input would increase this gap to $2.06 \text{ Gmol yr}^{-1}$, suggesting that a dominant sink of dissolved Zn has been overlooked by Little et al. (2014). Recently, Little et al. (2016) have identified and quantified another sink for dissolved Zn through preservation in the sediments near the continental margins ($0.56 \text{ Gmol yr}^{-1}$), which can fill the gap projected by Little et al. (2014). However, even with this new output, accounting for the hydrothermal activity in the overall input fluxes, yet, projects a missing sink for the oceanic dissolved Zn (missing output flux = $1.50 \text{ Gmol yr}^{-1}$).

As mentioned above, this sink can be the preservation of biogenic particle-associated Zn in the deep sea sediments. Bruland et al. (1994) estimated $1.2\text{-}2.4 \text{ Gmol yr}^{-1}$ for such sink, when updated by other sinks considered by Little et al. (2014) and (2016), the total sink can be $2.11\text{-}3.31 \text{ Gmol yr}^{-1}$. The new input flux estimated in our study ($2.41 \pm 0.5 \text{ Gmol yr}^{-1}$) is consistent with this output flux. Note that in order to interconvert the residence times and input/output

fluxes, we apply 5.4 nmol/kg as the mean oceanic concentration of dissolved Zn (Chester and Jickells, 2012) and 1.35×10^{21} kg as the total mass of the world oceans (Baumgartner et al., 1975).

From a removal perspective, similar to other nutrients, more efficient biogenic particle production can increase the removal efficiency of dissolved Zn (Bruland et al., 1994) and hence decreases its residence time and oceanic mean concentration (i.e. inventory). The productivity of the ocean can change markedly on glacial/interglacial timescales, for example, due to variability of nutrient availability in the surface ocean. Martínez-García et al. (2014) have documented a rise in the surface ocean productivity during the Last Glacial Maximum (LGM), corresponding to higher dust input to the Southern Ocean. Shorter residence time of a nutrient can give rise to more rapid decrease of inventory after the removal efficiency increases, assuming the same extent of input. Inasmuch as the dissolved Zn inventory is mostly controlled by hydrothermal activity and hydrothermal activity fluctuates within a millennial timescale, the input fluxes of dissolved Zn to the ocean may not change significantly within a glacial/interglacial timescale, suggesting a possible rapid drop in oceanic dissolved Zn inventory during more productive oceanic intervals. In contrast, despite the recent appraisal of hydrothermal and sedimentary impacts (Elrod et al., 2004; Resing et al., 2015), dust is one of the major dissolved Fe sources to the ocean which can change the total input of dissolved Fe dramatically within glacial/interglacial timescales (Conway and John, 2014b). Such variability among the dominance of trace metal sources and their fluctuation timescale can cause substantial changes in the degree of availability of trace metals compared to each other with time, which can be influential on the biogeochemistry of the ocean.

Dissolved Zn distribution shows one of the most remarkable surface-to-deep and deep North Atlantic-to-deep North Pacific gradients among the trace metals (Bruland, 1980; Wyatt et al., 2014; Roshan and Wu, 2015), indicating an efficient biological pump that transports dissolved Zn from the surface to the deep ocean through uptake and remineralization processes. Even though we observe a significant hydrothermal source of dissolved Zn to the deep ocean, dissolved Zn generally correlates with Si, which is predominantly sourced from rivers (Frings et al. 2016) in most of the world oceans (Bruland, 1980; Wyatt et al., 2014; Roshan and Wu, 2015). This indicates that the biologically-driven internal turnover (surface to deep) of dissolved Si and Zn in the ocean, which probably controls the Zn:Si correlation, is much more efficient than the boundary inputs of these elements to the ocean (i.e. rivers for Si and hydrothermal vents for Zn). The highly dynamic internal cycling of dissolved Zn and Si in the ocean can envelop the effect of diverse external sources on the general correlation between these two elements to some extent. As shown in Figure 2b, although we estimated a substantial hydrothermal flux for dissolved Zn, the regeneration-controlled background of dissolved Zn largely overwhelmed the hydrothermal signal.. This indicates that for trace elements which have an efficient internal cycling, capturing and quantifying the external sources (i.e. boundaries) require accurate and precise sampling and analytical methods.

4. Conclusion

Dissolved Zn concentration was determined in seawater samples collected in the tropical South Pacific. Although an enrichment of silicate as a Zn-correlated property is observed along the transect within the depth range of the East Pacific Rise (i.e. 2300-2800 m), the component of dissolved Zn which is in excess to silicate based upon the Zn-Si relationship shows a remarkable enrichment within the mentioned zone. This excess Zn shows a distal transport to the central South Pacific with a pattern similar to that of ^3He within 2300-2800 m depth. This indicates that hydrothermal-derived Zn mixes with surrounding waters conservatively. The slope of the excess Zn- ^3He relationship and the global efflux of mantle-derived ^3He allow for the calculation of $1.75 \pm 0.35 \text{ Gmol yr}^{-1}$ as the global input flux of dissolved Zn from hydrothermal activities. This flux is many times higher than the flux due to fluvial input and dust deposition, suggesting that mantle-derived Zn dominates the oceanic dissolved Zn inventory. Considering this hydrothermal flux, dissolved Zn remains in the ocean with a residence time much shorter than previously thought.

Even though it has not been well-studied, sedimentary input can be an appreciable source of dissolved Zn. Recent studies have highlighted sedimentary inputs by demonstrating “hotspots” of dissolved Zn concentration near the boundaries of the North Atlantic Ocean (Conway and John, 2014a; Roshan and Wu, 2015). This potential source of dissolved Zn has to be constrained in the future studies. Furthermore, despite an invariant ratio of Zn to mantle-derived ^3He within our basin-wide survey, this ratio can be different in other hydrothermal systems. Finding the ratio in the Atlantic Ocean is rather difficult. However, since its impact on the global ^3He flux is $\sim 25\%$ of the flux in the Pacific (Bianchi et al., 2010), a 4-fold higher ratio in Atlantic hydrothermal systems can lead to a dissolved Zn hydrothermal flux similar to that of the Pacific.

The hydrothermal fields located in the Indian Ocean and the Southern Ocean have to be studied for their dissolved Zn input flux as well.

Appendix A

Supplementary material related to this article can be found online at <address provided by journal for supplementary material>

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